

# Research progress on bio-based thermosetting resins

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## Abstract

Compared with the rapid progress on bio-based thermoplastics, research on bio-based thermosetting resins should have attracted much more attention, considering that they will have a bright future. In this paper, the current research progress on bio-based thermosetting resins is reviewed. We pay special attention to the synthesis and investigation of properties of epoxies and unsaturated polyesters derived from renewable plant oil, cardanol, rosin acid, lignin, glycerol, gallic acid, furan, isosorbide, itaconic acid, etc. This mini review gives an overall perspective for bio-based thermosets.

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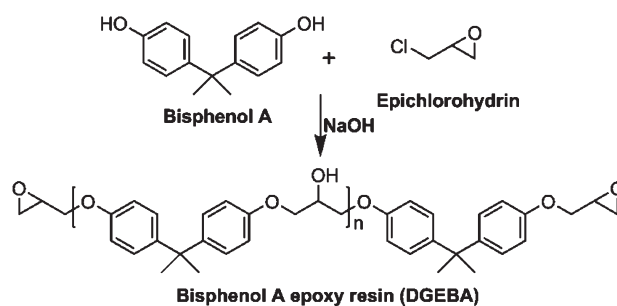
**Keywords:** bio-based thermosetting resins; epoxy; unsaturated polyesters

## INTRODUCTION

Nowadays, driven by the pressure from environmental pollution concerns and crude oil shortage, more and more attention has paid to the conversion of renewable biomass into useful polymeric materials and composites. The development and use of bio-based materials are regarded as an effective way to save petroleum resources and protect our living environment. Up to now, large quantities of bio-based thermoplastics, such as poly(lactic acid), polyhydroxyalkanoates and poly(butylene succinate), have been synthesized and commercialized successfully.<sup>1–3</sup> However, compared with the rapid progress on bio-based thermoplastics, much less research has been done on bio-based thermosetting resins. Thermosetting resins, also known as thermosets, are chemical materials in liquid, soft solid or viscous state that can be changed irreversibly into infusible and insoluble polymer networks by curing reactions. Due to their high modulus, high strength and good thermal and chemical resistances, thermosetting resins have been widely used in coatings, adhesives, composites, electronic packaging, etc. Among all the polymeric materials produced, thermosetting resins account for 18% by weight.<sup>4</sup> Therefore, research on bio-based thermosetting resins should attract much attention and will have a bright future. In fact, several kinds of thermosets derived from biomass have been reported. In this paper, the research progress on bio-based thermosets, especially bio-based epoxy resins and unsaturated polyesters, is reviewed.

## BIO-BASED EPOXY RESINS

Epoxy resins, as prepolymers with at least two epoxide groups, account for approximately 70% of the market of thermosetting resins. Diglycidyl ether of bisphenol A (DGEBA; shown in Fig. 1), which represents more than 90% of the epoxy precursors in the world, is by far the most widely used monomer to formulate epoxy networks.<sup>5</sup> DGEBA can be synthesized from epichlorohydrin and bisphenol A in the presence of sodium hydroxide as



**Figure 1.** Synthetic route to bisphenol A epoxy resin (DGEBA).

shown in Fig. 1. Although epichlorohydrin can be made from bio-based glycerol according to the Solvay Epicerol<sup>®</sup> and Dow GTE technologies,<sup>6,7</sup> bisphenol A, accounting for more than 67% of the molar mass of DGEBA,<sup>8</sup> is totally derived from fossil resources. In addition, bisphenol A has been reported to be hazardous to infants and young children. Several developed countries have recently banned its use in food contact materials, especially baby bottles.<sup>9,10</sup> Considering the principle of bio-based materials or green chemistry, there has been increasing interest in recent years in developing bio-based epoxy resins as alternatives to DGEBA, as shown in Fig. 2.

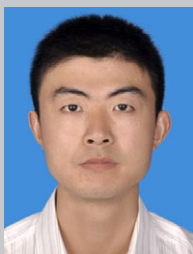
Plant oils have been widely used as the starting materials for surfactants, cosmetic products, lubricants, coatings and resins. Due to its triglycerides that contain C=C double bonds, plant

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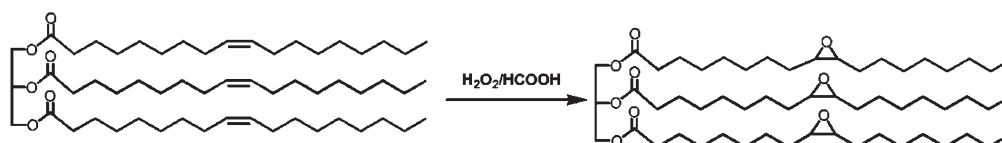
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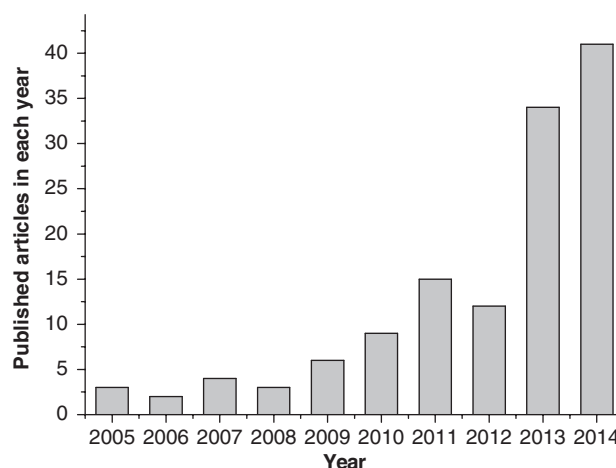
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oil can be converted to epoxy resin by the epoxidation reaction with molecular oxygen, and also to peroxide by chemo-enzymatic reactions.<sup>11,12</sup> The common synthetic route of plant oil-based epoxy resins is shown in Fig. 3.



**Figure 3.** Synthesis of plant oil-derived epoxy resins.

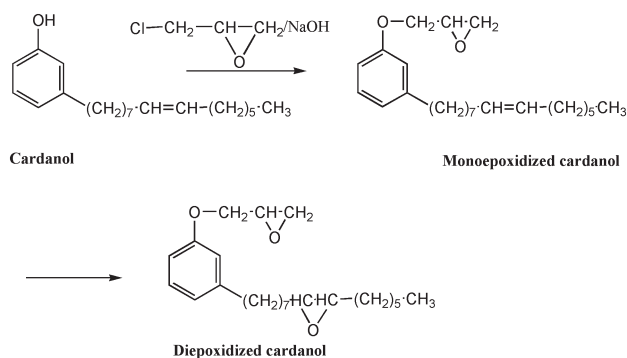


**Figure 2.** Published articles on bio-based epoxy resins each year from 2005 to 2014 (based on search result from Web of Sciences).

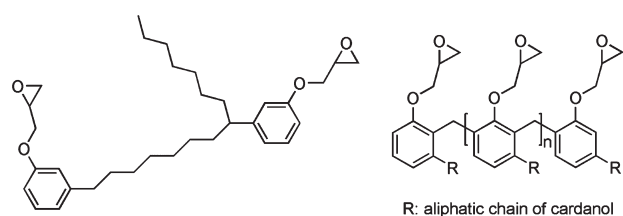
A commercially available and extensively used plant oil-derived epoxy resin is epoxidized soybean oil (ESO), which is mainly used as a plasticizer and stabilizer for poly(vinyl chloride), pigment dispersion agent and chemical intermediate, and in lubricants and cutting oils. The long flexible chains and relatively low reactivity of epoxy groups of ESO always lead to poorly crosslinked materials with unsatisfactory thermal or mechanical properties. In order to improve the properties of ESO networks, petroleum-based epoxy resin (bisphenol A epoxy resin) is usually employed to modify ESO-based systems.<sup>13,14</sup> Generally speaking, a higher epoxy value will lead to a higher glass transition temperature ( $T_g$ ) as well as hardness of the epoxy resin. Thus, the plant oil-based epoxy resins with high functionality derived from linseed oil usually possess higher  $T_g$  and better mechanical properties. However, in order to obtain cured systems with satisfactory performance, rigid curing agents or comonomers are necessary.<sup>15–17</sup> In addition, loading with fillers or fibers is also a common method to reinforce plant oil-based epoxy resins.<sup>18–20</sup>

Cardanol, extracted from cashew nut shell liquid, is another renewable resource of immense potential.<sup>21</sup> Patel *et al.*<sup>22</sup> synthesized a difunctional cardanol-based epoxy resin using a two-step method. As shown in Fig. 4, the phenolic hydroxyl group was substituted by epichlorohydrin at first, and then the double bonds were epoxidized further. The obtained diepoxidized cardanol was used as a reactive diluent for DGEBA/anhydride systems. Cardolite Company, the world's largest cardanol producer, focused only on products from cashew nut shell liquid. Difunctional and multifunctional epoxy resins (Fig. 5) derived from cardanol have been produced.<sup>23</sup> Due to the flexible aliphatic chains, they are mainly used as toughening agents for other brittle epoxy resins and as self-toughening epoxy resins.

Rosin is another abundantly available natural product, with a global annual production of about 1.2 million tons. It contains various isomerized acids ( $C_{19}H_{29}COOH$ ; >90%) and some

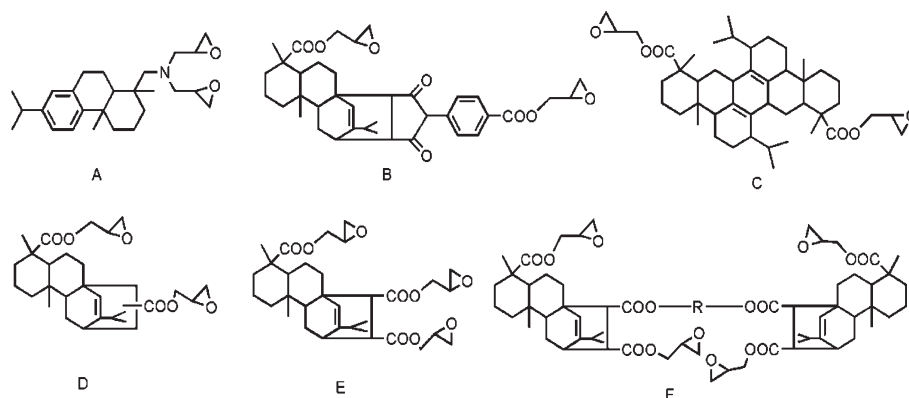


**Figure 4.** Synthesis of diepoxidized cardanol.<sup>22</sup>

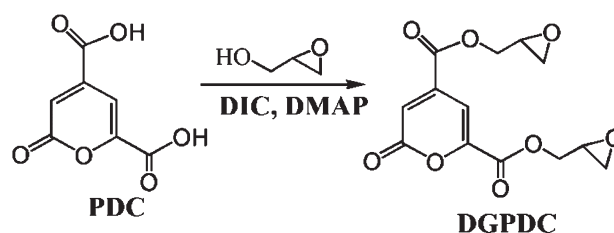


**Figure 5.** Commercially available difunctional and multifunctional cardanol-based epoxies.<sup>23</sup>

neutral substances.<sup>24</sup> Rosin acids are similar to cycloaliphatic or aromatic compounds in molecular rigidity. Thus, many efforts have been made to develop epoxy resins from rosin acids for the sake of getting a suitable alternative to DGEBA.<sup>25–31</sup> Mono-functional rosin-based epoxy directly synthesized from rosin acid and epichlorohydrin, and difunctional and multifunctional rosin-based epoxies derived from derivatives of rosin, such as dehydroabietylamine, rosin diacid, maleopimaric acid and polymerized rosin, have been reported.<sup>25–27,32–34</sup> (Fig. 6). The cured rosin-based epoxy resins often show higher  $T_g$  and comparable mechanical properties relative to cured DGEBA. However, due to their rigid hydrogenated phenanthrene ring structures, the rosin-based epoxies usually demonstrate serious brittleness. In order to overcome this disadvantage, Deng *et al.*<sup>31</sup> chemically incorporated flexible siloxane chains into the rosin-based epoxy systems and Wang *et al.*<sup>35</sup> introduced flexible polycaprolactone into the rosin-based anhydride-type curing agents. The results showed that the brittleness could be relieved to a certain degree



**Figure 6.** Chemical structures of rosin-based epoxy resins: A,<sup>25</sup> B,<sup>27</sup> C,<sup>32</sup> D,<sup>33</sup> E,<sup>26</sup> F.<sup>34</sup>



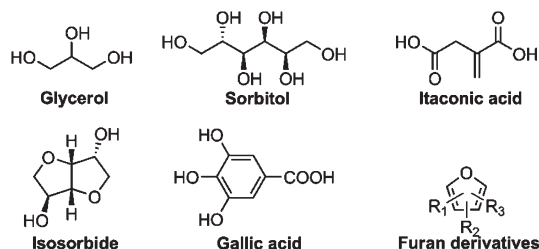
**Figure 7.** Synthesis of bio-based epoxy resin from lignin-derived PDC.

after the introduction of soft segments. Inevitably, their thermal and mechanical properties were greatly compromised.

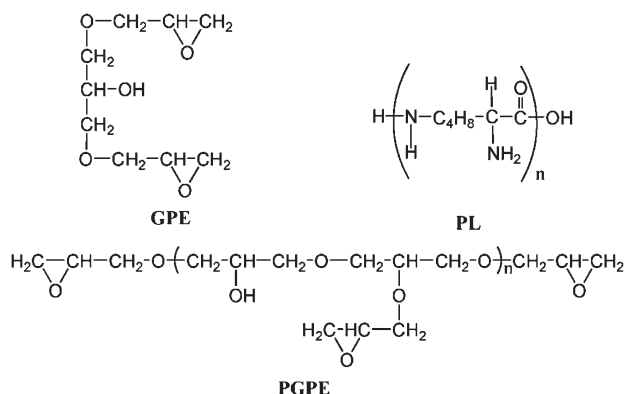
Lignin, one of the most abundant renewable resources second only to cellulose, is a large and complex natural polymer. It possesses many hydroxyl groups and phenolic hydroxyl groups, which can be converted to reactive epoxy groups directly by the reaction with epichlorohydrin. The resulting epoxy resins usually exhibit low curing reactivity and unstable properties because of the low mobility of the macromolecular species and complex structures.<sup>36,37</sup> And they also present relatively low compatibility with curing agents and even could not be dissolved in common solvents. Thus, instead of lignin itself, its derivatives with relatively low molecular weight have become a popular feedstock for the synthesis of epoxy resins. Guo *et al.*<sup>38</sup> prepared a relatively stable epoxy resin from sodium lignin sulfonate. And Zhao *et al.*<sup>39</sup> synthesized two kinds of epoxy resins (liquid epoxy resin and solid epoxy resin) from the phenolated product of lignosulfonate. Otsuka *et al.*<sup>40</sup> reported the efficient production of 2-pyrone-4,6-dicarboxylic acid (PDC) from lignin. Using lignin-derived PDC as the starting material, Hasegawa *et al.*<sup>41</sup> synthesized an epoxy resin by reacting PDC with 2,3-epoxy-1-propanol as shown in Fig. 7. Cured with the same curing agents, the epoxy from PDC showed higher tensile strength than DGEBA.

In addition to the renewable resources mentioned above, many potential platform monomers (Fig. 8), such as glycerol, sorbitol, isosorbide, gallic acid, itaconic acid and furan, obtained from biomass by chemical processes or biological fermentation, have also been reported as the starting materials for the synthesis of epoxy resins.

Both glycerol from the transesterification of plant oil and sorbitol from the reduction of hexose (a byproduct of the starch industry) are bio-based platform chemicals and are abundant resources.



**Figure 8.** Chemical structures of bio-based platforms for epoxy resins.



**Figure 9.** Chemical structures of glycerol polyglycidyl ether (GPE), polyglycerol polyglycidyl ether (PGPE) and  $\epsilon$ -poly(L-lysine) (PL).

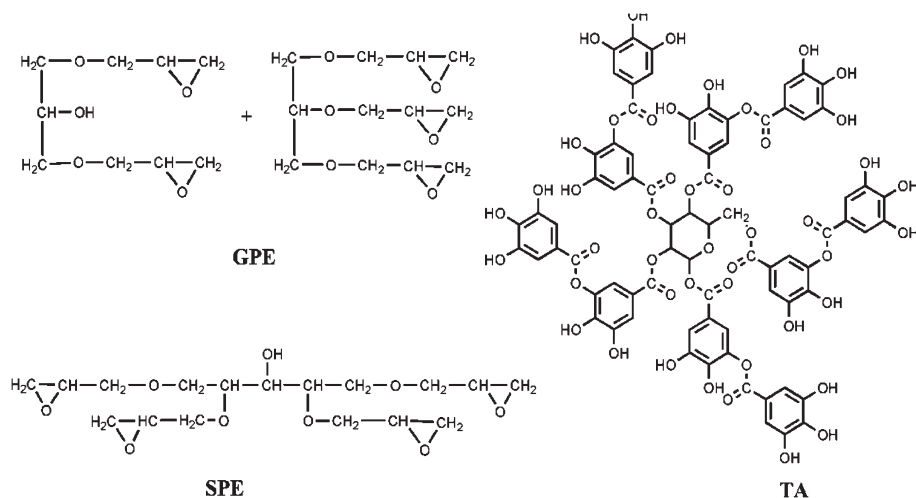
Nowadays, several epoxy resins derived from bio-resourced glycerol and sorbitol, such as glycerol polyglycidyl ether (GPE), polyglycerol polyglycidyl ether (PGPE) and sorbitol polyglycidyl ether (SPE), are industrially available according to Nagase ChemteX Corp.<sup>42,43</sup> However, their flexible structures usually lead to low  $T_g$  and it is difficult for them to be used as structural materials. Takada *et al.*<sup>42</sup> cured GPE and PGPE with  $\epsilon$ -poly(L-lysine) (Fig. 9). The cured systems exhibited poor mechanical properties with a tensile strength of 3.98 MPa, modulus of 5.73 MPa and  $T_g$  of 47 °C. In order to obtain a satisfactory performance, rigid tannic acid (TA) was employed as a curing agent to cure GPE in the work of Shibata and Nakai<sup>43</sup> and the crosslinked GPE/TA system showed much higher  $T_g$  of 97.9 °C. They also prepared epoxy networks by

curing SPE with TA (Fig. 10). Due to the higher functionalities of SPE, the SPE/TA networks presented an even higher  $T_g$  of 115.9 °C and better mechanical properties.

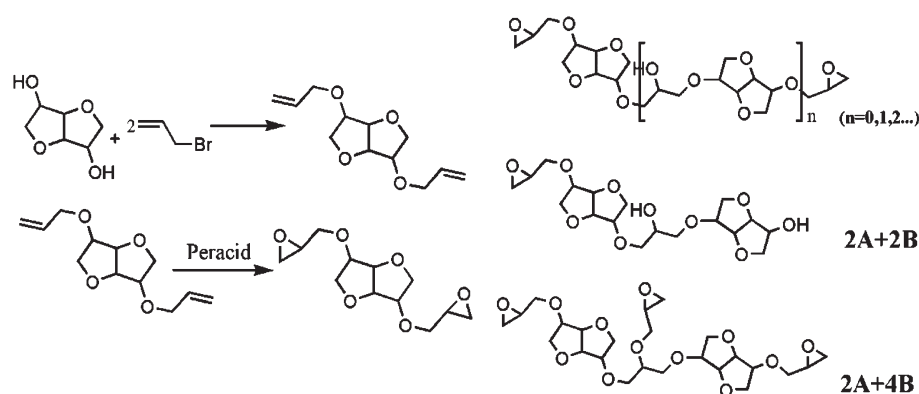
Chrysanthos *et al.*<sup>44</sup> synthesized two kinds of epoxy resins from isosorbide, DGEDAS<sub>0</sub> and DGEDAS<sub>n</sub>, via two different epoxidation methods (Fig. 11) and their properties were investigated. Compared with DGEBA, these two bio-based epoxy resins showed higher curing reactivity when cured using isophoronediamine (IPDA). However, the DGEDAS<sub>0</sub>/IPDA and DGEDAS<sub>n</sub>/IPDA systems showed  $T_g$  of 112 and 96 °C, respectively, which are much lower than that of the DGEBA/IPDA system (155 °C). The reason might be that the aliphatic ring structure in isosorbide is not as rigid as the aromatic one in DGEBA.

Gallic acid, also known as 3,4,5-trihydroxybenzoic acid, is widely present both free and as part of hydrolysable tannins in gallnuts, sumac, tea leaves, oak bark and other plants.<sup>45,46</sup> The presence of benzene ring, phenolic hydroxyls and carboxyl group makes it very similar to bisphenol A, the currently predominant monomer for epoxy synthesis. Therefore, gallic acid has been employed as an alternative to bisphenol A for the synthesis of epoxy resins (GEGA)<sup>47–49</sup> (Fig. 12). Due to its high functionality,  $T_g$  of cured GEGA (233 °C) is 73 °C higher than that of the DGEBA network (160 °C) when cured using the same curing agent. In addition to being a good candidate to replace DGEBA or improve thermal and mechanical properties of conventional epoxy systems, the bio-based GEGA could also be used as a reactive dispersant for graphene modification by strong  $\pi-\pi$  interactions.<sup>49</sup> It can play dual roles in graphene/epoxy composites: (1) promoting the dispersion of graphene in the epoxy matrix and (2) serving as a linkage between graphene and epoxy network for enhancement of properties.

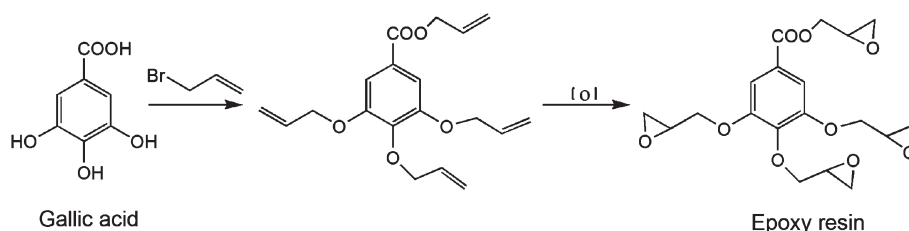
Furanyl building blocks are also regarded as promising alternatives to petroleum-based phenyl building blocks in thermosetting resin synthesis because of their aromatic characteristics and ready availability. Up to now, furaldehyde as well as furfuryl alcohol derived from hemicelluloses have been widely used for furan resin synthesis. Recently, furan derivatives (Fig. 13) have also been selected as viable starting materials for high-performance epoxy resins.<sup>50–53</sup> For example, Zhang *et al.*<sup>50</sup> produced a series of epoxy resins from furanyl amine, which demonstrated good mechanical and thermal properties as well as good adhesion and reactivity. Liu and co-workers<sup>51</sup> synthesized an epoxy monomer starting



**Figure 10.** Chemical structures of sorbitol polyglycidyl ether (SPE) and tannic acid (TA).



**Figure 11.** Synthetic route to isosorbide diglycidyl ether via allylic derivative (left) and structures of isosorbide diglycidyl ether via epichlorohydrin (right).

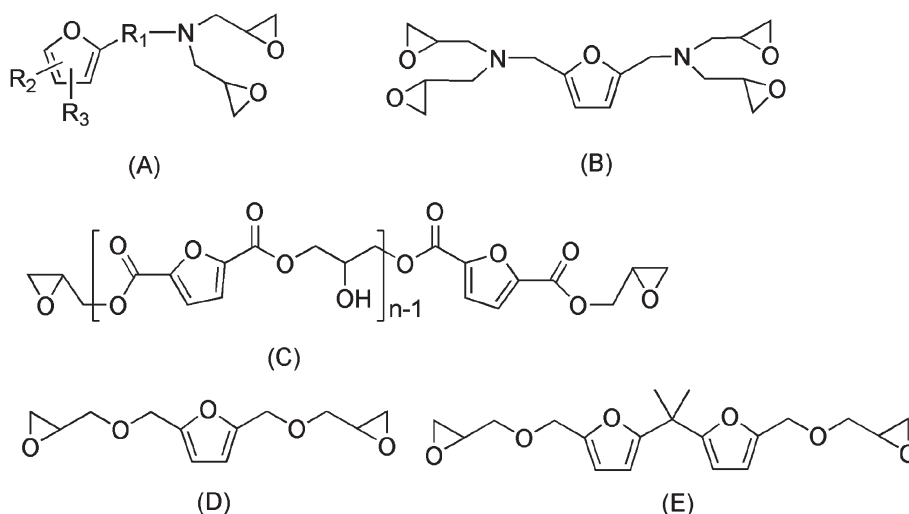


**Figure 12.** Synthesis of gallic acid-based epoxy resin.

from 2,5-furandicarboxylic acid.<sup>54</sup> Cho *et al.*<sup>52</sup> synthesized several furan-based epoxies and evaluated their potential use in the adhesive industry. Hu *et al.*<sup>53</sup> compared the properties of furanyl-based epoxies and their phenyl-based counterparts after being cured with the same amine curing agents. The results showed that the furan-based epoxy resins possessed higher  $T_g$ , strength and modulus.<sup>52,53</sup>

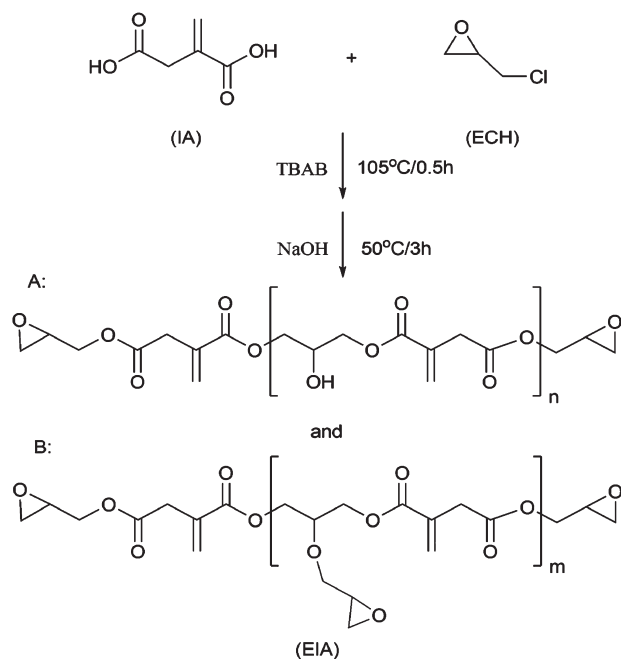
Itaconic acid, or methylenesuccinic acid, is produced by fermentation of carbohydrates, such as glucose, using *Aspergillus terreus*. It has been shown to be an excellent comonomer<sup>55,56</sup> and is widely used as the primary source for emulsion paints<sup>57</sup> and paper coating latexes.<sup>58</sup> The carboxyls in its copolymers can also be grafted with epoxy groups by esterification with epichlorohydrin, and the obtained functional copolymers used to enhance the mechanical properties of DGEBA.<sup>59</sup> Itaconic acid

can directly react with epichlorohydrin to form an epoxy resin (EIA) containing double bonds.<sup>8</sup> The synthetic scheme is shown in Fig. 14. EIA has a higher epoxy value (0.625) and higher reactivity than DGEBA. After a cure reaction with methylhexahydrophthalic anhydride, EIA networks show comparable or even better tensile strength (87.5 MPa), flexural strength (152.4 MPa) and modulus (3430.8 MPa) as well as  $T_g$  (130 °C) relative to the DGEBA networks. Due to the presence of carbon–carbon double bonds, EIA network rigidity and toughness can be manipulated further by introducing rigid or soft comonomers. The carbon–carbon double bond of itaconic acid can also be converted into an epoxy group. Therefore, a trifunctional itaconic acid-based epoxy monomer (TEIA) having high epoxy value (1.16) and low viscosity (0.92 Pa s, 25 °C) was synthesized following the route shown in Fig. 15.<sup>60</sup> Owing to its high epoxy value and unique structure,



**Figure 13.** Chemical structures of epoxies from furan derivatives: A and B,<sup>50</sup> C,<sup>51</sup> D and E.<sup>52,53</sup>





**Figure 14.** Synthesis of itaconic acid-based epoxy resin (EIA) with carbon–carbon double bonds.<sup>8</sup>

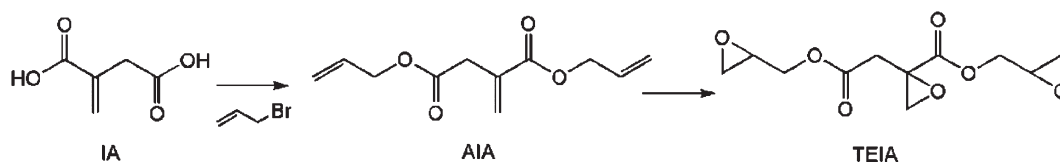
comparable or better mechanical properties as well as higher  $T_g$  can be obtained for the TEIA network relative to the DGEBA network. Meanwhile, TEIA systems exhibit much lower viscosity than the DGEBA system, which indicates that TEIA systems might have better processability. Thus, TEIA has a great potential for use as a high-performance epoxy resin. In addition, the

itaconic acid-based epoxy resin was further functionalized using 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide as shown in Fig. 16.<sup>61</sup> As a matrix, the cured EADI showed  $T_g$  and mechanical properties comparable to those of DGEBA as well as excellent flame retardancy with UL94 V-0 grade during vertical burning tests. As a reactive flame retardant, it showed good flame-resistant effect on the DGEBA system.

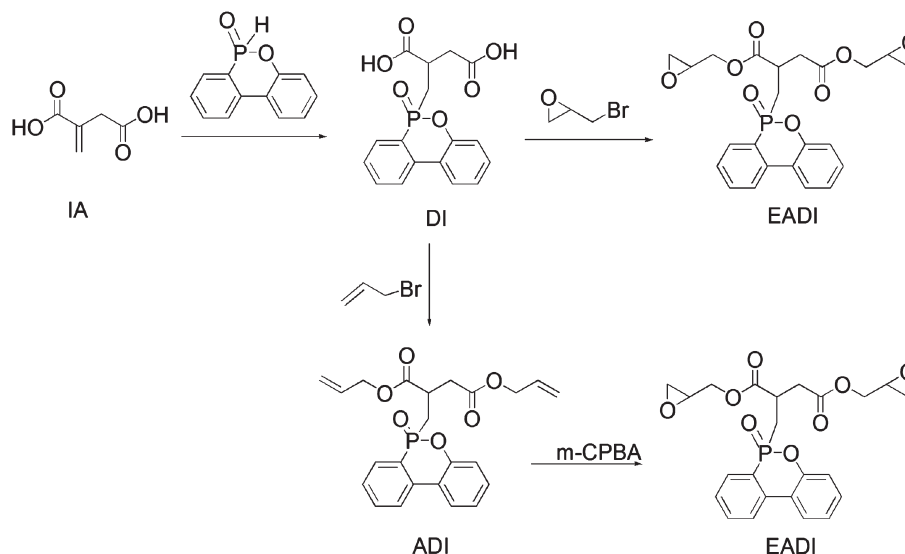
## BIO-BASED UNSATURATED POLYESTERS

Unsaturated polyesters (UPEs) are copolyesters prepared by condensation of a saturated dicarboxylic acid or its anhydride as well as an unsaturated dicarboxylic acid or anhydride (usually maleic anhydride) with one or more dialcohols, such as ethylene glycol or propylene glycol, as shown in Fig. 17. After the ester condensation reaction, the remaining carbon–carbon double bonds are capable of free radical polymerization to form a highly crosslinked network. UPEs are commonly used in fiberglass composites, sheet molding compounds and bulk molding compounds. They have enjoyed a long-term leadership in petroleum-based composites since 1941 due to their low cost, ease of handling and good balance of mechanical, electrical, chemical and fire-resistance properties.<sup>62,63</sup>

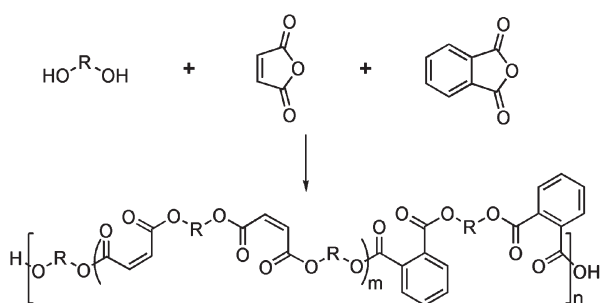
In recent years, bio-based diacids and diols containing unsaturated bonds have usually been employed to prepare bio-based UPEs. Itaconic acid has two carboxyl groups and one carbon–carbon double bond in its molecular structure, which makes it very similar to maleic acid. Therefore, as a potential alternative to maleic acid and maleic anhydride, itaconic acid has been used to synthesize bio-based UPEs.<sup>64–68</sup> Through the condensation reaction between 1,4-butanediol, succinic acid and itaconic acid or maleic acid, reactive carbon–carbon double bonds were introduced into the main chain of poly(butylene



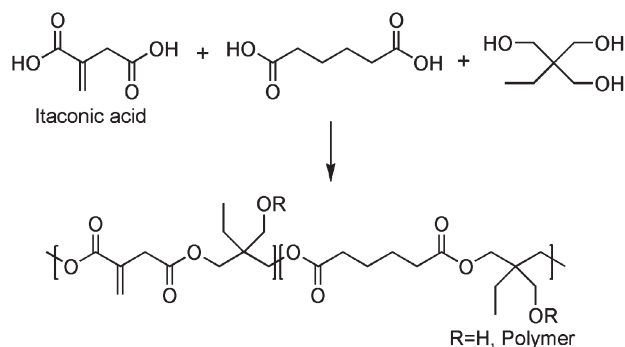
**Figure 15.** Synthesis of trifunctional itaconic acid-based epoxy resin (TEIA).<sup>60</sup>



**Figure 16.** Synthesis of phosphorus-containing itaconic acid-based epoxy resin (EADI).<sup>61</sup>

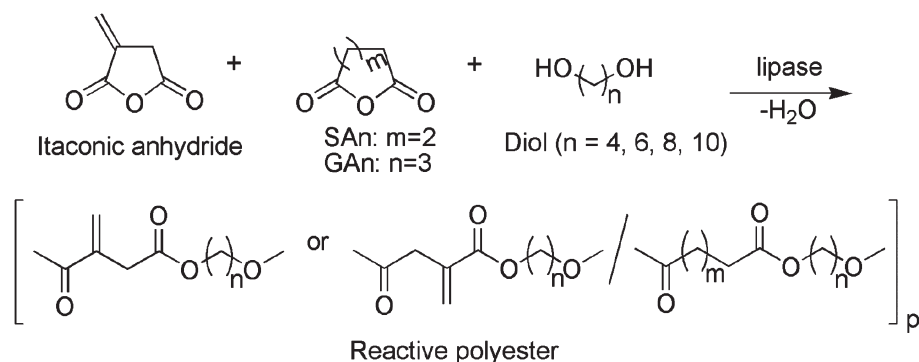


**Figure 17.** Synthetic route to unsaturated polyesters.

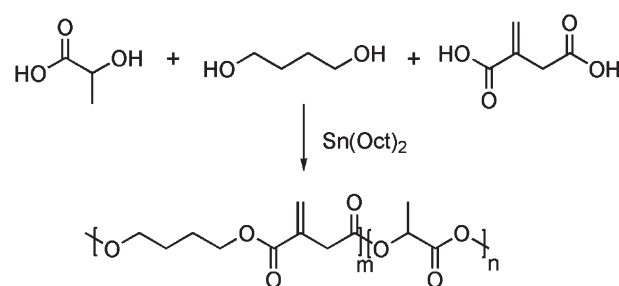


**Figure 18.** Synthesis of itaconic acid-based unsaturated polyester.<sup>66</sup>

succinate) prepolymers.<sup>64</sup> After they were cured at 115 °C in the presence of benzoyl peroxide, the resulting networks were insoluble in chloroform, while retaining some biodegradability. Itaconic acid-based polyesters can be also cured using photoinitiation. As shown in Fig. 18, Barrett *et al.*<sup>66</sup> obtained polyesters from itaconic acid by direct polycondensation. When they were subjected to photocuring reaction, the crosslinked systems exhibited Young's modulus, ultimate tensile stress and rupture strain values of 0.17–398.14 MPa, 0.11–18.20 MPa and 5–198%, respectively. As we know, compared with thermoplastics, the cytotoxicity of thermosets is minimal, which makes them excellent candidates as future biomaterials. In the work of Sakuma *et al.*,<sup>65</sup> itaconic acid-based polyesters were copolymerized with methacrylate-substituted polysilsesquioxane to fabricate bio-based organic–inorganic composites for bioengineering and their biocompatibilities were investigated. Itaconic anhydride was also used to synthesize UPEs.<sup>69–71</sup> As shown in Fig. 19, Yamaguchi *et al.*<sup>70</sup> employed itaconic anhydride as a novel



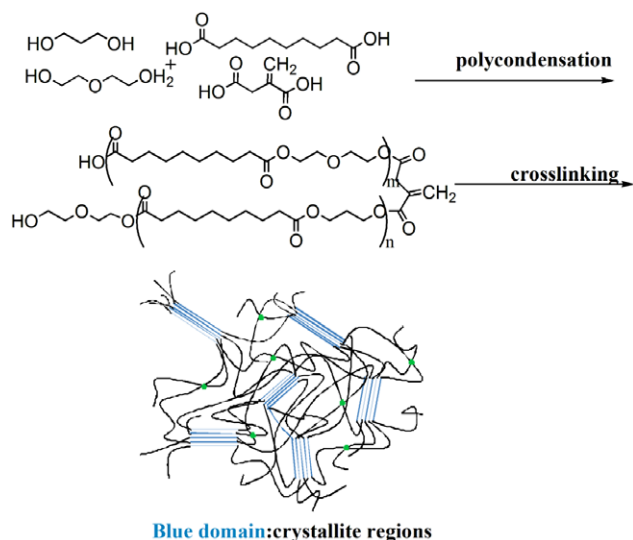
**Figure 19.** Lipase-catalyzed ring-opening addition condensation polymerization.<sup>70</sup>



**Figure 20.** Preparation of linear copolymer of D,L-lactic acid, 1,4-butanediol and itaconic acid.<sup>78</sup>

monomer for lipase-catalyzed ring-opening addition condensation polymerization involving dehydration to produce reactive polyesters.

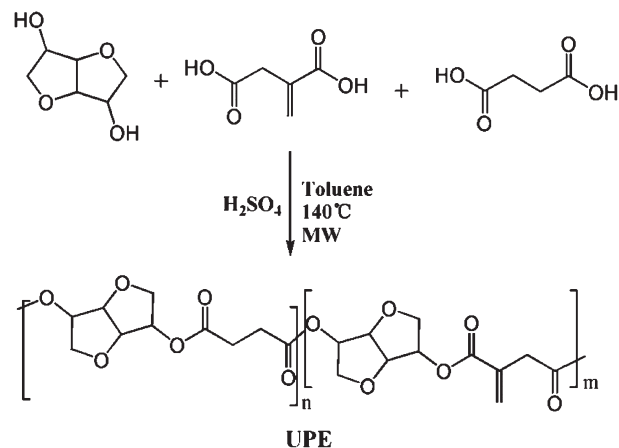
With the increasing interest in bio-based polymers and some governments' tax amnesty for bio-based materials depending on the bio-based content, attention has been directed at UPEs with high bio-based content.<sup>72–78</sup> Fully bio-based unsaturated aliphatic polyesters were successfully prepared by *Candida antarctica* lipase B (CALB)-catalyzed polycondensations of succinate, itaconate and 1,4-butanediol. The cured UPEs were brittle materials with Young's modulus, ultimate tensile stress and rupture strain of 11–66 MPa, 3–12 MPa and 26–34%, respectively.<sup>72</sup> Dai *et al.*<sup>73</sup> prepared a series of fully bio-based UPEs from itaconic acid and bio-based diols. Waterborne UV-curable coatings based on these UPEs exhibited high hardness, good water resistance and solvent resistance. They also used the bio-based UPEs to enhance the properties of acrylated epoxidized soybean oil (AESO), the bio-based UPEs showing good compatibility with AESO. The tensile strength, modulus,  $T_g$  and bio-based content of the AESO-based thermosetting resins were significantly improved after the introduction of the synthesized UPEs. In addition, the modified AESO systems could be well coated on the surface of tinplate and glass plate and good coating properties, such as hardness, flexibility, adhesion, solvent resistance and water absorption, were demonstrated.<sup>74</sup> Researchers also introduced itaconic acid or itaconic anhydride into poly(lactic acid) to obtain UPEs.<sup>71,78</sup> Ramo *et al.*<sup>78</sup> synthesized an unsaturated copolymer via the polycondensation of lactic acid, 1,4-butanediol and itaconic acid as shown in Fig. 20. Elastomers could be obtained by controlling the itaconic acid component in polyesters.<sup>75,77</sup> Wei *et al.*<sup>75</sup> synthesized UPEs from bio-based monomers in large-scale production, such as sebacic acid, itaconic acid, succinic acid, 1,3-propanediol and 1,4-butanediol, through melting polycondensation. Bio-based



**Figure 21.** Preparation of crosslinked bio-based polyester and its structure.<sup>77</sup>

elastomer nanocomposites with high performance were obtained after introducing silica nanoparticles followed by chemical crosslinking. Guo *et al.*<sup>77</sup> used 1,3-propanediol, sebacic acid and itaconic acid as the main raw materials for the synthesis of bio-based poly(propylene sebacate) as shown in Fig. 21. Diethylene glycol was used to tailor the flexibility of the polyesters. The crosslinked polyesters (elastomers) were found to be promising shape memory polymers with excellent shape recovery and fixity (near 100% and independent of thermomechanical cycles).

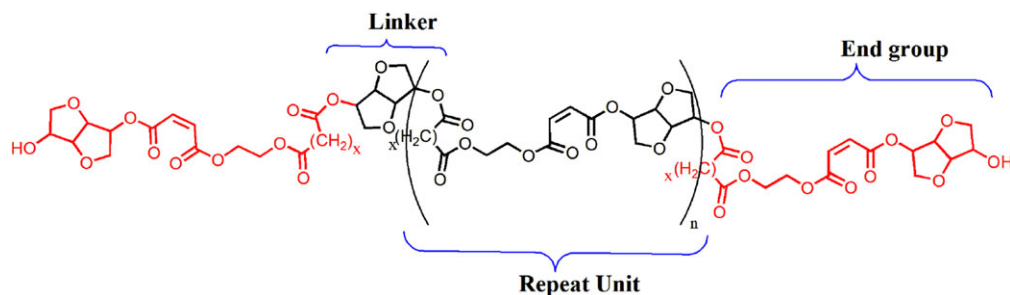
In order to obtain bio-based UPEs with high performance, rigid bio-based compounds such as isosorbide have also been employed.<sup>76,79,80</sup> Polycondensation of isosorbide with itaconic acid and succinic acid was performed in the presence of sulfuric acid as a catalyst in toluene at around 140 °C under microwave irradiation, as shown in Fig. 22.  $T_g$  of the polyesters based on isosorbide, itaconic acid and succinic acid were found to vary from 57 to 65 °C. After the polyesters were crosslinked radically with dimethyl itaconate, the  $T_g$  values were slightly increased to about 74 °C.<sup>76</sup> Sadler *et al.*<sup>79,80</sup> prepared a series of bio-based UPEs from isosorbide, ethylene glycol and maleic anhydride as the source of C=C double bonds, and oxalic acid, malonic acid, succinic acid, adipic acid, suberic acid and sebacic acid as the secondary diacid, as shown in Fig. 23. When they were blended with styrene, resins were obtained possessing viscosities (120–2200 cP) amenable to a variety of liquid molding techniques. After curing



**Figure 22.** Synthesis of unsaturated polyester (UPE) from isosorbide, itaconic acid and succinic acid.<sup>76</sup>

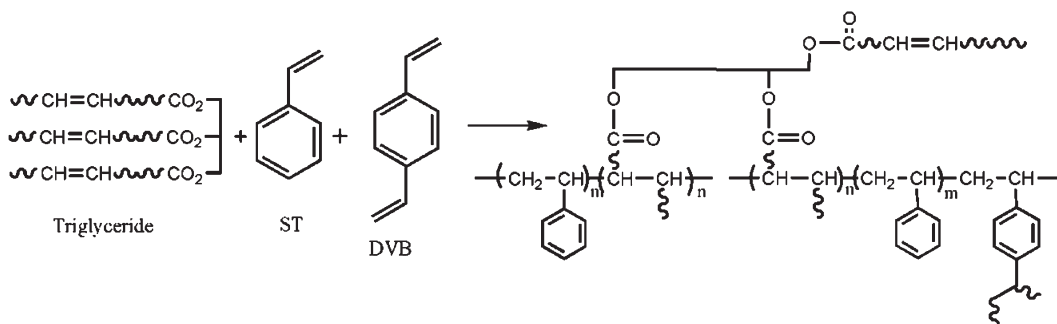
reaction, the resulting network demonstrated  $T_g$  (53–107 °C) and storage modulus (430–1650 MPa) that were in the desired range for composites manufacture.

Plant oils are predominantly made up of triglycerides containing C=C double bonds, allylic carbons and ester groups, which makes them very similar to synthesized UPEs. Li *et al.*<sup>81</sup> and Li and Larock<sup>82</sup> developed thermosets by the cationic copolymerization of soybean oil and corn oil with styrene and divinylbenzene, as shown in Fig. 24. These polymers have  $T_g$  varying from approximately 0 to 105 °C, which are comparable to those of conventional rubbers and plastics. Because of the low reactivity of C=C double bonds in the triglycerides, they are often epoxidized in the presence of peroxide followed by the ring-opening esterification of the epoxide groups with acrylic acid to introduce more reactive C=C double bonds, as shown in Fig. 25. The most popular and commercially available plant oil derivative is AESO.<sup>46,63,73,74,82–88</sup> However, due to the long flexible aliphatic chain of soybean oil, petroleum-based rigid compounds such as cycloaliphatic epoxy resin,<sup>83</sup> styrene and divinylbenzene<sup>82,84,88</sup> and sol–gel silica<sup>85</sup> are often used to copolymerize with AESO to achieve the necessary rigidity and strength for some end applications. To develop high bio-based content thermosets from plant oil, increasing efforts have been made to explore bio-based comonomers or crosslink agents to replace the petroleum-based rigid compounds.<sup>46,73,74,86</sup> In the work of Liu and co-workers, derivatives of rosin acids, gallic acid as well as itaconic acid were used to modify and strengthen plant oil-based polyesters. UPEs with more bio-based content and better properties were obtained.

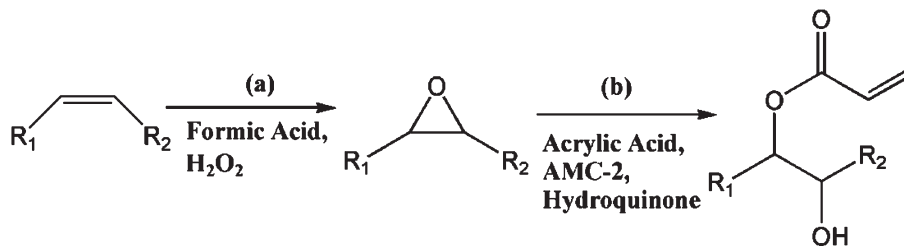


**Figure 23.** Chemical structure of bio-based unsaturated polyester containing isosorbide.<sup>79,80</sup>





**Figure 24.** Preparation of thermosets by the cationic copolymerization of plant oil, styrene (ST) and divinylbenzene (DVB).



**Figure 25.** Synthetic route to acrylated epoxidized plant oil.<sup>88</sup>

## CONCLUSIONS AND PERSPECTIVES

Research on bio-based epoxy resins and unsaturated polyesters has developed significantly over the past few years due to the great potential to replace their petroleum-based counterparts. In recent years, exploiting bio-based thermosetting resins with better properties and higher bio-based content has been the main objective of our work. However, compared with the rapid progress on bio-based thermoplastics and considering the increasing requirements for special applications, functionalized bio-based thermosets with unique properties, such as flame retardancy, shape memory and self-healing, should be designed and developed in the future. In addition, the higher price and limited availability of raw materials for bio-based thermoset synthesis are also key problems to be addressed before their widespread utilization.

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